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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : DAIDO STEEL CO LTD

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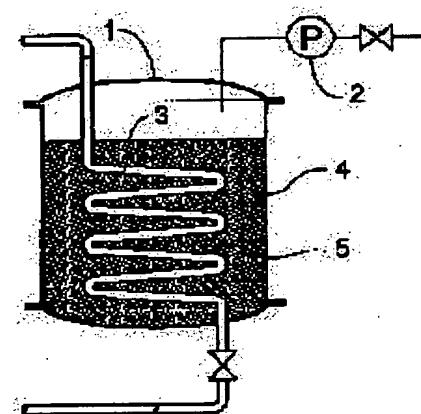
(72)Inventor : SAITO MAKOTO  
SHIMIZU TAKASUMI

## 1) ABSORPTION AND RELEASE OF HYDROGEN AND VESSEL FOR STORING HYDROGEN

## 1)Abstract:

ROBLEM TO BE SOLVED: To reduce the amount of heat supply to a stem at the time of absorption and release of hydrogen and further the anty of heat required for removal by filling the peripheries of hydrogen sorption alloy grains filled in a vessel with a thermal buffering substance ving a melting point within a specific range and utilizing the latent heat the melting and solidification of the thermal buffering substance caused the absorption and release of the hydrogen.

DLUTION: Hydrogen absorption alloy grains 4 having the surface coated th a metal selected from Pb, Pt, Rh, Ir, Au, Ag, Cr, Ni, Co, Cu and T1 are ed in a vessel 1 equipped with a coil 3 and void parts thereof are then ed with a thermal buffering substance 5 having -10 to +100° C melting int. Hydrogen is then absorbed thereon at normal temperatures and the rmal buffering substance is subsequently solidified with endothermic at generated at this time to suppress a temperature increase in the ssel 1. A pump 2 is then operated to reduce the pressure in the vessel to release the hydrogen. The thermal buffering substance is subsequently melted with the exothermic heat generated at the time. hereby, the absorption and release of 1mol hydrogen based on 1g hydrogen absorption alloy can be carried out at a temperature within the nge of 0 to 50° C.



## GAL STATUS

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AIMS

## laim(s)]

laim 1] The circumference of the particle of the hydrogen storing metal alloy with which it was filled up in the  
ntainer is filled with the heat buffer matter with the melting point of the range of -10 to 100 degrees C. The  
sorption-discharge method of the hydrogen characterized by mitigating supply of the heat to the system at the time  
absorption-discharge of hydrogen, and the initial complement of removal of the heat from a system by generation of  
at accompanying absorption of hydrogen carrying out melting of the heat buffer matter, and using the latent heat in  
process in which the endothermic accompanying discharge of hydrogen makes the heat buffer matter solidify.

laim 2] as a particle of a hydrogen storing metal alloy, it is \*\*\*\*\* about the particle of an alloy, or the front face of  
powder-compacting Plastic solid from Pd, Pt, Rh, Ir, Au, Ag, Cr, nickel, Co, Cu, and Tl -- the absorption-discharge  
method of the hydrogen of the claim 1 which uses what was covered with the metal

laim 3] as heat buffer matter, it is \*\*\*\*\* from water, a cyclohexane, benzene, para xylene, a biphenyl, a  
phenylmethane, and a triphenylmethane color -- the absorption-discharge method of the hydrogen of the claim 1  
which uses a thing

laim 4] The hydrogen storage container which is filled up with the particle of a hydrogen storing metal alloy in the  
ntainer which offered a means to have offered a means to introduce and emit hydrogen gas, and to heat and cool the  
terior, and comes to fill the opening section of a particle with the heat buffer matter which has the melting point in  
the range from -10 degrees C to 100 degrees C.

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## TAILED DESCRIPTION

## Detailed Description of the Invention]

01]

[the technical field to which invention belongs] this invention relates to the hydrogen storage container for enforcing absorption-discharge method of having used the hydrogen storing metal alloy and method of hydrogen.

02]

[description of the Prior Art] As an alloy with a large hydrogen-absorption property, LaNi5, LaCo5, MmNi5 (mixture of the rare earth metal to which Mm is called "misch metal"), TiFe, TiMn1.5, Mg2 Cu, or Mg2 nickel is known. Promising \*\* of the absorption-discharge using these alloys of hydrogen gas is carried out as technology in which the conventional high-pressure bomb becomes unnecessary, and various research and development are being done.

03] Anyway, generation of heat produces the absorption-release reaction of the hydrogen by the hydrogen storing metal alloy M in hydrogen absorption as follows, and heating is seen in hydrogen desorption.

04]  $M + H \rightleftharpoons MH + Q$  -- various directions, such as operating cold energy as heat pump which raises temperature to elevated temperature from OK and low temperature, are considered from the source of high temperature using this property

05] On the other hand, when using a hydrogen storing metal alloy as a storage means of hydrogen, it is necessary to remove promptly the heat which removed promptly the heat generated with absorption, and was absorbed with discharge hydrogen, and to suppress change of the temperature of a system small. Otherwise, the elevated temperature to which equipment exceeds durable temperature will be reached, or discharge of hydrogen will stop.

06] As a solution of this problem, many pipes for in-and-out of hydrogen gas were prepared conventionally, a metal is attached in a container wall, or the coil which lets the heat carrier for heating-cooling pass is prepared. However, hydrogen storing metal alloy collapses by the volume change by which it is usually used with powder so that easily, if movement of hydrogen is repeated while also using a granular thing, and becomes an impalpable powder, and once a powdered thing does not have good heat conduction, \*\*\*\* is not fundamental [ these cures ].

07]

[problem(s) to be Solved by the Invention] The purpose of this invention is by carrying out the absorption relief of generation of heat and the endothermic accompanying absorption-discharge of hydrogen on the spot to offer the equipment used for operation of the absorption-discharge method that heat conduction of hydrogen storing metal alloy wider mitigated the problem of not being good and method of hydrogen.

08]

[means for Solving the Problem] The absorption-discharge method of the hydrogen of this invention fills with the heat buffer matter with the melting point of the range of -10 to 100 degrees C the circumference of the particle of the hydrogen storing metal alloy with which it was filled up in the container. It is characterized by mitigating supply of the heat to the system at the time of absorption-discharge of hydrogen, and the initial complement of removal of the heat from a system by generation of heat accompanying absorption of hydrogen carrying out melting of the heat buffer matter, and using the latent heat in process in which the endothermic accompanying discharge of hydrogen makes the heat buffer matter solidify. Here, the particle of a hydrogen storing metal alloy is a meaning which includes both aggregated particles obtained by carrying out compacting of powder and the powder.

009] The hydrogen storage container of this invention for enforcing this method As shown in drawing 1, a pump (2) offered on the means and concrete target which introduce and emit hydrogen gas. And it is the hydrogen storage container which is filled up with the particle (4) of a hydrogen storing metal alloy in a means to heat and cool the interior, and the container (1) which specifically offered the coil (3), and comes to fill the opening section of a particle with the heat buffer matter (5) which has the melting point in the range from -10 degrees C to 100 degrees C.

010] As a hydrogen storing metal alloy, the alloy of said various composition can use it arbitrarily. Since the

nponent of oxidizing qualities, such as O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S, may often mix as an impurity as for the inside hydrogen gas, a hydrogen storing metal alloy may oxidize by it and performance degradation may be seen. The applicant proposed previously the metal which bears the front face of the particle of a hydrogen storing metal alloy at dization, and specifically covering with the coat of a gill \*\*\*\*\* metal from Cr, Pd, Pt, Ag, Au, Rh, Ir, and Tl as to cure (JP,5-40036,B). This technology is applicable also to this invention.

[11] As heat buffer matter, the matter which has the melting point is used for the range of -10 degrees C - 100 degrees C as mentioned above. It is possible to operate in the temperature field which exists within limits which can be the speed of the absorption-release reaction of hydrogen so that I may be understood by that cause from the operation which carries out a postscript, and description of an effect. The following matter is mentioned as an example. (the inside of a parenthesis is the melting point)

water (0 degree C)

cyclohexane (6.2 degrees C)

benzene (5.5 degrees C)

p-xylene (16 degrees C)

phenylmethane (26.3 degrees C)

phenyl (70.5 degrees C)

phenylmethane color (93 degrees C)

[12]

[Invention and Effect] since hydrogen desorption is endothermic reaction when making the hydrogen stored with reduced pressure emit supposing it heats a system with a heat carrier and raises to the temperature region beyond the melting point or, supposing a system is in a state higher than the melting point of the heat buffer matter, where hydrogen is absorbed now, the temperature of a system falls. The situation is expressed with lower right direction from points of the graph of drawing 2 as change which meets the other line. If the temperature of a system falls and it falls in the melting point M of the heat buffer matter, the solidification of this matter starts, and the temperature of a system will be maintained by discharge of the latent heat for a while. If the solidification of the heat buffer matter finishes, the temperature of a system will fall and go again.

[13] Absorption of hydrogen takes place to the above and reverse. That is, by raising the hydrogen partial pressure of a system, absorption of the hydrogen by the hydrogen storing metal alloy starts, and generation of heat is seen. The temperature of a system is maintained by M points until melting of the heat buffer matter which went up toward the upper right from the B point of drawing, and had been solidified starts and all fuse temperature mostly in connection with it. When melting finishes, the temperature of a system is the other side to elevation again.

[14] Thus, since the temperature of a system is maintained in absorption-discharge of hydrogen the part which can be the latent heat of the dissolution-solidification of the heat buffer matter, and near the melting point of the matter according to this invention, the amount of heat with required giving a system, in order to urge discharge or absorption of hydrogen, or removing can be lessened, and stable operation is attained. Therefore, the means of heating-cooling which a hydrogen storage container should offer has been the thing of small capacity enough more, and cost can be lowered down by both sides of an installation cost and running cost.

[15]

[example] TiMn1.5 Pd coat with a thickness of about 1 micrometer was formed in the front face of the powder of 100 meshes of average grain size of an alloy by electroless deposition. The container which offered the coil which lets the heat carrier for heating-cooling pass for this inside was filled up, and distilled water which carried out degasifying was led.

[16] Occlusion of the hydrogen was first carried out in ordinary temperature, the heat generated with a heat carrier in that case was removed, and elevation of the temperature in a container was suppressed by 50 degrees C. Then, it was compressed and hydrogen was made to emit. In the meantime, supply of the heat by the heat carrier was not performed, but temperature left for falling. Although solidification started in the place which descended at 0 degree C, there was no parenchyma top problem in discharge of hydrogen.

[17] Next, the heat carrier was sent to the container which emitted hydrogen and water has solidified, and some water was dissolved. Hydrogen gas was made to press fit and absorb in the state. By generation of heat accompanying absorption, while water ran [ \*\*\*\* and absorption ], the temperature in a container was kept at about 0 degree C, and elevation of temperature started after the whole melting.

[18] Thus, absorption-discharge of 0.1 mols [ per 1g of hydrogen storing metal alloys ] hydrogen was able to be reformed in the 0-50-degree C temperature requirement.

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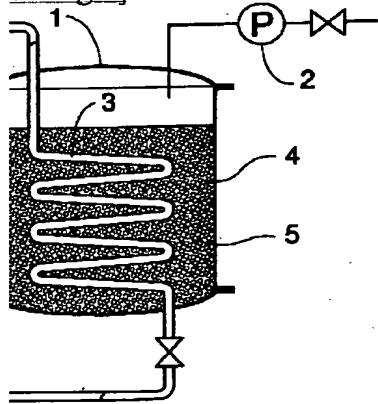
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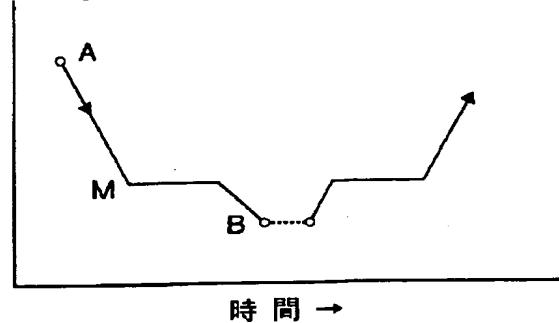
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## AWINGS

[awing 1]



[awing 2]



[anslation done.]

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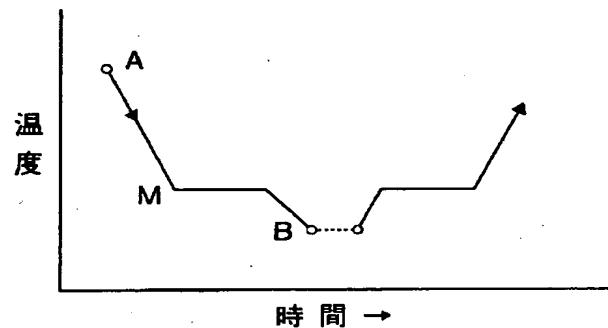
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(54)【発明の名称】 水素の吸収-放出方法および水素貯蔵容器

(57)【要約】

【課題】 水素吸蔵合金を利用して水素の吸収-放出を行なうに当り、吸収-放出反応による発熱および吸熱を補償するための、外部からの冷却および加熱の負担を軽減する。

【解決手段】 水素貯蔵容器内に充填した水素吸蔵合金の粒子の間隙を、水、シクロヘキサン、p-キシレンのような、-10°C~100°Cの間に融点を有する熱緩衝物質で満たし、その融解-凝固の潜熱を利用する。



る。具体例としては、つきの物質が挙げられる。(カッコ内は融点)

水 (0°C)

シクロヘキサン (6. 2°C)

ベンゼン (5. 5°C)

p-キシレン (16°C)

ジフェニルメタン (26. 3°C)

ビフェニル (70. 5°C)

トリフェニルメタン (93°C)

#### 【0012】

【作用および効果】いま、水素を吸収した状態で熱緩衝物質の融点より高い状態に系があるとすると、(または系を熱媒体により加熱して、融点以上の温度域に高めたとすると)、減圧により貯蔵されている水素を放出させるとき、水素放出は吸熱反応であるから、系の温度は低下する。その様子は、図2のグラフのA点から右下方に向う線に沿う変化としてあらわされる。系の温度が低下して熱緩衝物質の融点Mに至ると、この物質の凝固が始まり、しばらくの間は潜熱の放出によって系の温度が保たれる。熱緩衝物質の凝固が終ると、再び系の温度は低下して行く。

【0013】水素の吸収は、上記と逆に起る。すなわち、系の水素分圧を高めることにより水素吸蔵合金による水素の吸収が始まり、発熱をみる。それに伴って、温度は図のB点から右上に向って上昇し、凝固していた熱緩衝物質の溶融がはじまり、ほぼ全部が溶融するまで、系の温度はM点に維持される。溶融が終ると、系の温度は再び上昇に向う。

【0014】このようにして、本発明によれば、水素の吸収-放出に当って、熱緩衝物質の融解-凝固の潜熱が利用できる分、その物質の融点付近に系の温度が維持されるため、水素の放出または吸収を促すため系に与え、または除くことが必要な熱の量を少なくすることができます、安定な操業が可能になる。したがって、水素貯蔵

容器がそなえるべき加熱-冷却の手段がより小容量のもので足り、設備費、運転費の両面でコストを低く抑えることができる。

#### 【0015】

【実施例】TiMn<sub>1.5</sub>合金の平均粒度100メッシュの粉末の表面に、無電解メッキによって厚さ約1μmのPd被膜を形成した。これを内部に加熱-冷却用の熱媒体を通すコイルをそなえた容器に充填し、脱ガスした蒸留水を満たした。

【0016】まず常温で水素を吸蔵させ、その際に熱媒体により発生する熱を除去して容器内の温度の上昇を50°Cまでに抑えた。続いて減圧して水素を放出させた。その間は、熱媒体による熱の供給は行なわず、温度が低下するにまかせた。0°Cに降下したところで凝固が始まったが、水素の放出に実質上問題はなかった。

【0017】次に、水素を放出して水が凝固している容器に熱媒体を送り、一部の水を融解させた。その状態で水素ガスを圧入し、吸収させた。吸収に伴う発熱で水が融け、吸収が進行する間、容器内の温度はほぼ0°Cに保たれ、全体の溶融後、温度の上昇が始まった。

【0018】このようにして、水素吸蔵合金1gあたり0.1モルの水素の吸収-放出を、0~50°Cの温度範囲において行なうことができた。

#### 【図面の簡単な説明】

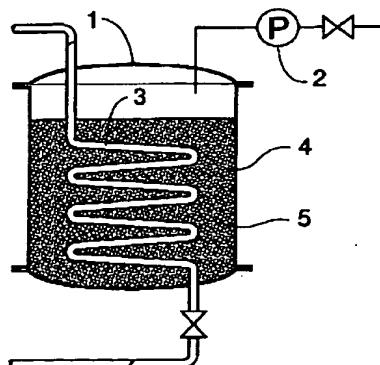
【図1】本発明の水素貯蔵容器の構成を概念的に示す縦断面図。

【図2】本発明の作用を説明するための、時間と系の温度との関係を示すグラフ。

#### 【符号の説明】

- 1 容器
- 2 水素ガスを導入および放出する手段(ポンプ)
- 3 加熱および冷却する手段(コイル)
- 4 水素吸蔵合金の粒子
- 5 熱緩衝物質

【図1】



【図2】

